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Arsonic & Arsinic Acids

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ARSONIC AND ARSINIC ACIDS

BY

SYLVESTER JOSEPH McGRATH

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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May 31, 1905

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Sylvester Joseph McGrath.

ENTITLED Arsonic and Arsinic Acids.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Science

H. S. Grindley.

HEAD OF DEPARTMENT OF General Chemistry.



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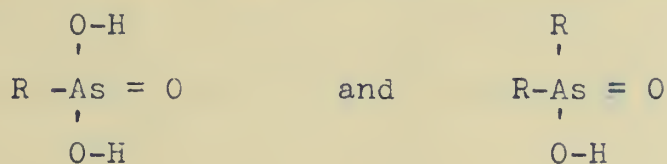
Arsonic and Arsinic Acids.

Arsonic acids may be considered derived from arsenic acid.

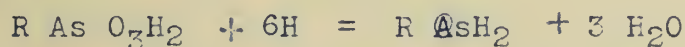
As $O(OH)_3$, by replacing one of the hydroxyl groups by a univalent hydrocarbon radicle or substituted radicle; thus the arsonic acids have the general formula $R As O(OH)_2$. Arsinic acids are dialkyl or dialkyl substitution products of arsenic acid and have the general formula $R R_1 As OOH$ where R and R_1 are any two, univalent hydrocarbon radicles. All of the arsinic acids prepared have the two radicles identical, except phenyl-p-toluyll cacodylic acid (Ann. Chem. (Liebig) 321, 157).

The arsinic acids may be considered homologous to cacodylic acid and are therefore frequently termed cacodylic acids - for instance, phenyl arsinic acid is also known as phenyl cacodylic acid.

The structural formulas usually assigned to the arsonic and arsinic acids are:

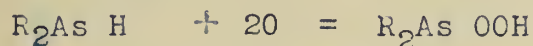
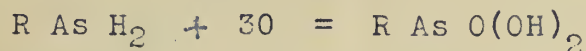


The best proof (Ann. Chem. (Liebig) 107, 269) of the direct union of the radicles with arsenic is seen in their reduction (Ber. d. chem. Ges. 27, 1378; American Chem. Journ. 33, 104) to the corresponding arsines, which unquestionably contain the radicles in direct union with arsenic:



The possibility here of molecular rearrangement is precluded by the fact that the arsines spontaneously reoxidize (American

Chem. Journ. 33, 124) to the corresponding acids:



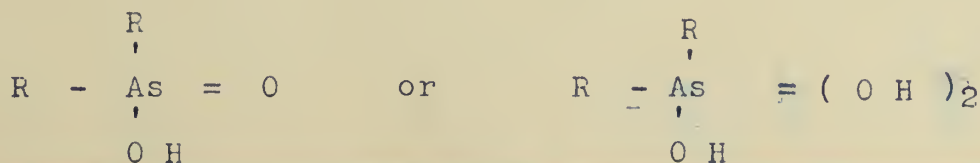
The proof of the pentavalence of the arsonic and arsinic acids is seen in their stability toward oxidizing agents (Eunsen, Ann. Chem. (Liebig) 46, 9; La Coste, Ibid, 208, 3, 32)- as for instance nitric acids or the halogens (La Coste and Michaelis, Ann. Chem. (Liebig) 201, 231.) All compounds known to contain trivalent arsenic are easily acted upon by halogens.

The remainder of the structure of the arsonic and arsinic acids is established by their basicity; the former are dibasic, (Ann. Chem. (Liebig) 107, 290: 320, 277), the latter are mono-basic, Baeyer concluded (Ibid. 107, 263) that cacodylic acid is analogous in structure to metaphosphoric acid, the $(\text{CH}_3)_2\text{As}$ group substituting the trivalent $\text{P} = \text{O}$ group and is thus in perfect concordance with the above structural formula. According to some recent work of Hantzsch (Ber. d. chem. Ges. 37, 1076), however, conductivity measurements of methyl arsinic acid, (cacodylic acid) tend to show that when treated with caustic alkali it does not react as a strictly mono-basic acid. Upon adding NaOH to a solution of sodium methyl arsinate the measurements show that the substance in solution is at least in part the sodium salt of a tribasic acid.

The author gives the following reaction as representing what takes place:

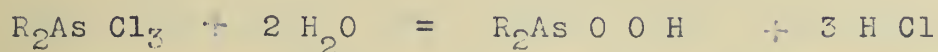
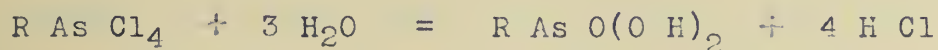


and thus the structural formula for the arsinic acids may be



the former bearing to the latter the same relation as ^{does} meta phosphoric acid to orthophosphoric acid.

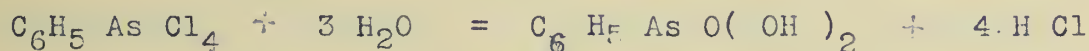
There is available at present only one good general method for the preparation of both arsonic and arsinic acids: viz,- the hydrolysis of the corresponding pentavalent radicle - halogen arsenic compounds:



The first application of this general reaction was made by Baeyer in the preparation of cacodylic acid (Ann. Chem. (Liebig) 107, 268),



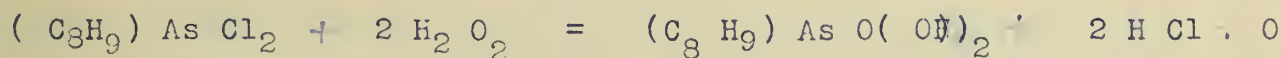
The first application in the aromatic series was made by La Coste and Michaelis (Ann. Chem. (Liebig) 201, 202), in the preparation of phenyl arsonic acid:



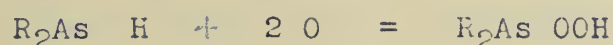
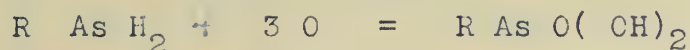
Modifications of the above general method are found in the oxidation of monomethyl arsenic dichloride by means of moist silver oxide (Ann Chem. (Liebig): 107, 236.):



the oxidation of m-xylyl arsenic dichloride by means of hydrogen peroxide (Ibid. 320, 333):

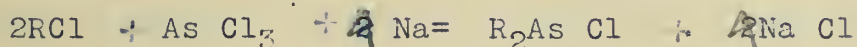


and the oxidation of primary (Ber. d. chem. Ges. 34, 3594; American Chem. Journ. 33, 124) and secondary (Ber. d. chem. Ges. 27, 1378; Wilcox thesis p) arsines by atmospheric oxygen, etc.:

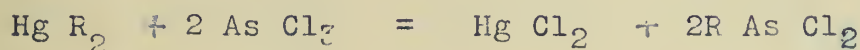


The intermediate compounds in the formation of the arsonic and arsinic acids; viz - the trivalent radicle - halogen compounds are derived by two general reactions:

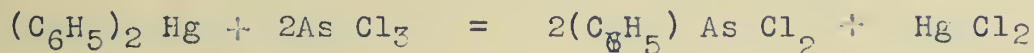
I. The condensation of arsenic trihalides and alkyl or alaryl mono halides by means of sodium:



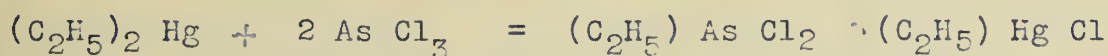
II. The interaction of arsenic trihalide and mercury alkyl or mercury alaryl:



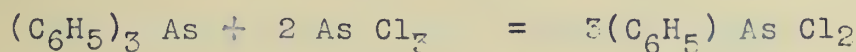
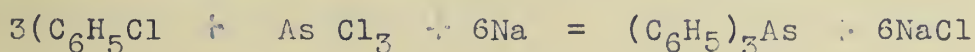
The first application of reaction I to the aromatic series was made by La Coste and Michaelis (Ann. Chem. (Liebig) 201, 196) in the preparation of phenyl arsenic dichloride:



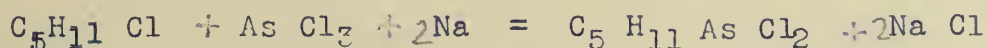
the first in the fatty series was made by La Coste (Ibid. 203, 33) in the preparation of ethyl arsenic dichloride:

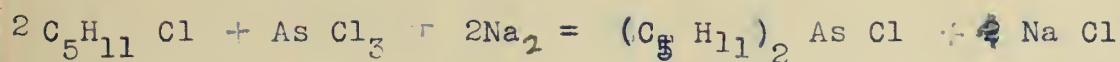


The first application of reaction (I) to the aromatic series was made by Michaelis and Rees (Ber. d. chem. Ges. 15, 2876) in the preparation of triphenyl arsine and its subsequent transformation to phenyl arsenic dichloride by heating with arsenic trichloride:



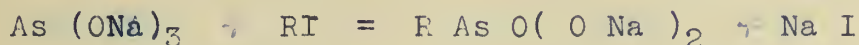
The first application of reaction (I) to the fatty series was made by Wilcox (Thesis on Secondary Arsine p ⁴⁹ -) in the preparation of mono- and di-isoamyl arsenic chlorides:





Besides the above general method for the preparation of arsonic and arsinic acids there are a number of special methods which are of great importance:

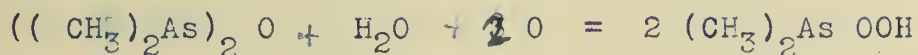
(1) - The reaction of alkyl halides with alkali arsenites to form fatty arsonic acids:



This reaction was first employed by Meyer (Ber. d. chem. Ges. 16, 1440), was modified by Klinger and Kreutz (Ann. Chem. (Liebig) 249, 147), and was elaborated and extended by Dehn (American Chem. Journ. 33, 131).

(2) - The Preparation of cacodylic oxide by heating potassium acetate and arsenic trioxide:

$4\text{C}_2\text{H}_3\text{CH}_2\text{OK} + \text{As}_2\text{O}_3 = ((\text{CH}_3)_2\text{As})_2\text{O} + 2\text{CO}_2 + 2\text{K}_2\text{CO}_3$ and its oxidation to cacodylic acid:



This reaction has not yielded a single homologue of cacodylic acid.

The arsonic acids hitherto known and studied are as follows:

1. Methyl
2. Ethyl
3. Phenyl
4. Nitro phenyl
5. Di methyl amido phenyl
6. p- Anisyl
7. p- Phenetyl
8. p- Benz

9. m-Benz⁹
10. Nitro benz¹⁰
11. O - Toluy¹¹
12. m. - " 12
13. p " 13
14. Nitro " 14
15. Benz " 15
16. O-Dimethyl amido-p-tolyl¹⁰
17. M-Xyl¹⁷
18. o- " 20
19. Monochlor Xyl¹⁸
20. Dichlor " 18
21. Nitro " 18
22. m- Tolu¹⁹
23. p- " 21
24. Phthalo¹⁹
25. Ps¹erdocumyl²²
26. p- Cumyl²²
27. Alpha Naphthyl¹⁶
28. Beta " 23
29. Tertiary butyl phenyl 24

(1)- Ber. d. chem. Ges.16, 1440; Ann. Chem. (Liebig) 107, 263;
249, 149. (2)- Ibid, 208, 34; American Chem. J. 33, 132.

(3)- Ann. Chem.(Liebig) 201, 203. (4)- Ber. d. chem. Ges. 27, 265.

(5)- Ann. Chem.(Liebig) 270. 139. (6) - Ber. d. chem. Ges. 20, 51.

(8) Ibid, 208, 3.

(7) - Ann. Chem.(Liebig) 320, 300. (9) - Ibid. 320, 329. (10) Ibid.

320, 325. (11) Ibid. 201, 255. (12).Ibid. 320, 328. (13) Ibid. 201,

255. (14) Ibid. 320, 321. (15) Ibid. 208, 3. (16) Ber. d. chem.

Ges.11, 1503. (17)- Ibid. 11, 1718. (18)- Ann. Chem.(Liebig)
320, 334. (19) - Ibid, 320, 335. (20) - Ibid, 320, 338.
 (21) - Ibid, 320, 339. (22)- Ibid, 320, 340. (23) -Ibid, 320,
 344. (24) - Ibid, 320, 342.

It will be seen that though some ²⁹arsinic acids of the aromatic
 series have been prepared only two of the fatty series have been
 prepared. I herein contribute two new fatty arsonic acids; viz-

30 . Propyl

31. Isoamyl

and also the aromatic arsonic acid,

32. Benzyl

The arsinic acids hitherto prepared and studied are the
 following:

1. Methyl
2. Ethyl ²
3. Phenyl ³
4. Benzyl ⁴
5. p, Toluy ⁵
6. Nitro phenyl ⁶
7. Benz ⁷
8. Phenyl-p-toluy ⁸
9. Isoamyl

(1)-Ann. Chem.(Liebig) 46, 2. (2) - Ibid, 92, 365. (3)-Ibid
201, 231; 321, 150. (4)- Ibid.233, 82. (5)- Ibid, 208, 20
 (6)- Ibid, 208, 25. (7)- Ibid, 321, 151. (8)- Ibid, 321, 157.
 (9)- Wilcox thesis p ⁵⁰.

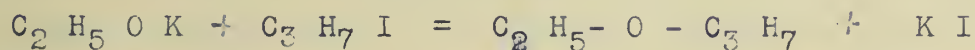
Normal Propyl Arsonic Acid.

This acid was prepared in the same manner as ethyl arsonic acid (American Chem. Journ. 33, 132). To 275 grams of arsenic trioxide (1 mol.), and 460 grams of potash (6 mols.), sufficient water was added to cause complete solution. After cooling, alcohol was added to the point of incipient precipitation of potassium arsenite, then 460 grams of normal propyl iodide (2 mols.) were added and the mixture was shaken. Usually either some potassium arsenite or some propyl iodide precipitates at this stage, but a homogenous solution may be produced by adding either water or alcohol or, when the solution is too concentrated, both must be added.

After keeping the mixture in tightly-stoppered bottles for a number of days, the following reaction:



and the unavoidable side-reaction:



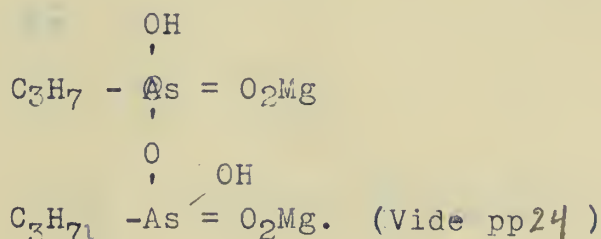
were complete. The mixture was then subjected to distillation to remove the alcohol and the ethyl-propyl ether.

Hydrochloric acid was added to the point of incipient precipitation; then a stream of chlorine was passed in until the pure white double-salt² first formed was dissolved and all of the iodine was precipitated. The filtrate was treated in the cold with magnesium mixture to precipitate the arsenate; upon boiling the filtrate from $\text{NH}_4\text{MgAsO}_4$ with more magnesium mixture the magnesium salt of normal propyl arsonic acid was precipitated as pearly-white, soapy crystals; yield 42 %. The magnesium salt was dried and analyzed;

Salt dried at $100^0 - 105^0$ for 8 hours - $\frac{\% \text{ Mg.}}{11.9\%}$

Salt dried at 130 ⁰ - 140 ⁰ for 6 hours	-	<u>11.99</u> ^{% Mg.}
Salt dried at 135 ⁰ - 160 ⁰ for 4 hours	-	12.09
Salt dried at 190 ⁰ - 200 ⁰ for 5 hours	-	13.38
Theory for (C ₃ H ₇ AsO ₃ Mg) ₂ H ₂ O - - - - -	--	12.05
Theory for C ₃ H ₇ As O ₃ Mg - - - - -	-	12.48

These analyses indicate that the magnesium propyl arsonate, like magnesium ammonium arsonate (Zt.f. Anal. Chem. 10, 62.) dried above 100⁰, contains one molecule of water of crystallization to two molecules of the anhydrous salt. Drying above 190⁰ not only removed this water of crystallization from magnesium propyl arsonate but also partially decomposed the salt. The probable structural formula is:



Free n-propyl arsonic acid was prepared by treating the magnesium salt in the cold with the calculated quantity of concentrated sulphuric acid and then extracting with alcohol. Upon evaporating the alcoholic solution the acid is obtained as needle-form crystals.

The acid is very soluble in water; 100 parts of solution at 26⁰ containing 43 parts of acid. It is also very soluble in alcohol but insoluble in ether.

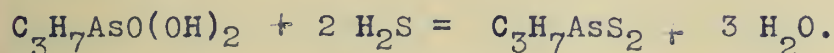
n-Propyl Arsenic Disulphide.

A quantity of the magnesium propyl arsonate was dissolved in dilute hydrochloric acid and was treated with hydrogen sulphide. A heavy, light-yellow oil was slowly precipitated. It was extracted with carbon bisulphide, dried with calcium chloride and freed from

the solvent by evaporation. .3196 grams substance gave .7176grams
 BaSO_4 Calculated for

	$\text{C}_3\text{H}_7\text{AsS}_2$	Found
S	35.16	35.29

The reaction therefore was :



The density of the disulphide was found to be 1.8. It is a heavy, viscid oil that becomes a gummy mass below -10° .

Isoamyl Arsonic Acid.

This acid was prepared in a manner nearly identical with manner of preparation of the n-propyl arsonic acid. One molecular quantity of arsenic trioxide (150 grams) was dissolved in six molecular quantities of potash (254 grams) and treated with two molecular quantities of isoamyl iodide (300 grams). The reaction mixture was permitted to stand for two or three days, when the alcohol was removed by distillation; the solution was then carefully neutralized and filtered from the double salt of $\text{As}_2\text{O}_3 \cdot 2\text{KI}$. Upon acidifying, a mass of shining, scale-like crystals separated, usually after some time; they were filtered off, washed, recrystallized, dried and analyzed. 0.3454 grams of the substance gave 0.1822 grams of water and 0.3383 grams of CO_2 .

Calculated for

	$\text{C}_5\text{H}_{11}\text{AsO}(\text{OH})_2$	Found
C	30.61	30.21
H	6.84	6.63

The magnesium salt was easily prepared by boiling the acid with magnesium mixture. Isoamyl Arsonic Acid is a pearly-white crystalline substance that melts at 194° ; one hundred c. c. of a saturated aqueous solution at 28° ...

contains 0.820 grams ; An equal quantity of a saturated alcoholic solution at 21° contains 2.2 grams. Like the other arsonic acids it is insoluble in ether.

Isoamyl Arsine Disulphide.

This sulphide was prepared as was the normal propyl disulphide.

It is a viscid light-yellow oil that will not solidify in a freezing mixture and cannot be distilled without decomposition.

0.2709 grams of the substance by the Carius method gave 0.6040 grams of BaSO₄

Calculated for

	C ₅ H ₁₁ As S ₂	Found
S	30.48	30.62

Benzyl Arsonic Acid.

Of all the arsonic acids benzyl is the most easily prepared.

When quantities of the substances indicated by the equation,



are dissolved in a mixture of alcohol and water in the manner previously described, freed from the alcohol by distillation, first neutralized and then carefully acidified with hydrochloric acid, a precipitation of benzyl arsonic acid to the extent of 60 % occurs.

Benzyl-ethyl ether equal to the loss of benzyl iodide not fixed by the arsenite may be recovered from the alcohol removed by distillation (Amer. Chem. Journ. 33, 142.). Upon washing the free acid with water and recrystallizing once from water or alcohol it is easily obtained pure.

.01828 grams of substance dried at 100° gave 0.2591 grams of

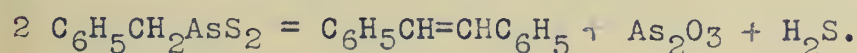
CO₂ and 0.0691 grams of H₂O.

	Calculated for	Found
	C ₆ H ₅ CH ₂ AsO(OH) ₂	
C	38.88	38.65
H	4.16	4.20

Benzyl arsonic acid crystallizes in long, beautiful, white, glistening needles. It melts at 167°. It dissolves with difficulty in cold water but is relatively, easily soluble in hot water; one hundred c. c. of a saturated aqueous solution at 22.5° contains 0.34 grams; at 27°, 0.39 grams; and at 97° contains 3.50 grams of the acid. Its solubility in alcohol is indicated by the following data: one hundred c. c. of saturated solution at 23° contains 0.87 grams and at 70°, 5.91 grams of acid. It is stable in the air and has no odor but a bitter, peculiar taste. It has an irritating effect upon the epidermis and the mucous membrane. An aqueous solution of the acid gives with silver nitrate a white precipitate of the silver salt; and with magnesium mixture on boiling, a white precipitate of the magnesium salt.

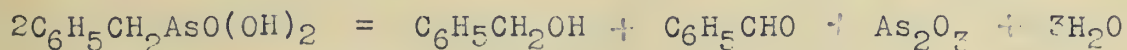
Benzyl Arsonic Disulphide.

Treated with hydrogen sulphide benzyl arsonic acid slowly precipitates the benzyl arsonic disulphide, C₆H₅CH₂AsS₂, which is very similar in properties to the disulphides described previously. It is a heavy, bright-yellow oil that dissolves rapidly in nitric acid liberating oxides of nitrogen and sulphur. On being heated alone it gives off hydrogen sulphide and forms arsenic trioxide and stilbene. The reaction is, probably :



Decomposition of Benzyl Arsonic Acid by Heat.

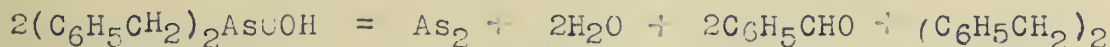
Benzyl arsonic acid on being heated yields the following decomposition products: benzyl alcohol, benzaldehyde, stilbene, water and arsenic trioxide. Probably the most important reaction is this;



Stilbene is formed according to the equation:



Upon heating the corresponding arsinic acid, $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{AsOOH}$, Michaelis and Paetow (Ann. Chem. 233, 83), found that benzyl arsinic acid probably decomposed according to the following reaction:



When fifty grams of benzyl arsinic acid, containing some water of crystallization was heated in a small flask attached to a condenser, an emulsion having the odor of benzaldehyde passed over. On standing, fifteen grams of water separated. The oil was shaken with a concentrated aqueous solution of sodium bisulphide until the odor of benzaldehyde was discharged; it was then extracted with ether.

The aqueous solution was easily proved to contain benzaldehyde sulphite by acidifying and distilling with steam. The ether solution, after drying with CaCl_2 , was distilled and gave fractions which boiled, largely, between 200 and 210° (Benzyl alcohol boils at 206°).

This portion was treated with acetyl chloride and benzoyl chloride and yielded, respectively, benzyl acetate (106°) and benzyl benzoate (324°). The amounts of benzyl alcohol and benzaldehyde produced were approximately equal; therefore the following reaction is established:

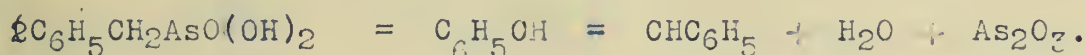


The higher fraction boiled largely between 300 and 310° (stilbene boils at 306° and dibenzyl boils at 284°). However, it was too small in quantity to be purified by fractionation and it could not be crystallized by cooling in a freezing mixture. A combustion gave:

	Substance	Calc. for stilbene	Calc. for dibenzyl	Calc. for benzyl alcohol.
C	84.65	93.34	92.30	77.07
H	7.95	6.66	7.70	7.64

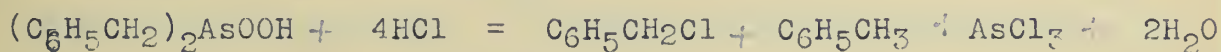
Evidently the higher fraction was a mixture of benzyl alcohol and stilbene rather than benzyl alcohol and dibenzyl. Further evidence of this is seen in its easy decolorization of bromine water.

Therefore a secondary decomposition of benzyl arsonic acid by means of heat is:



Decomposition of Benzyl Arsonic Acid by Acids.

Unlike its homologues and isologues benzyl arsonic acid is easily decomposed by mineral acids. Michaelis and Paetow¹ (Ann. Chem. 233, 84.), observed that concentrated hydrochloric acid decomposed dibenzyl arsinic acid completely into arsenic trichloride, benzyl chloride and toluene, according to the equation:



With concentrated hydrochloric I find that benzyl arsonic acid is decomposed into benzyl chloride and arsenious acid (no toluene was detected) therefore the reaction is this:



With sulphuric acid I find that dibenzyl, benzaldehyde, and arsenious acid are the decomposition products, therefore the following reaction is probable:



The speed of the above reaction may be determined, after treatment, by titration with a standard iodine solution, free iodine having no effect on arsonic acids. The accompanying table shows the great speed of the decomposition:

Wt. of benzyl Arsonic Acid.	cc., of H_2O	cc. of H_2SO_4	Time Minutes	Temperature	Percent Decomposition,
1.5 grams	25	10	30	100	100
1.5 "	25	10	15	100	100
1.318 "	25	5	5	100	99
1.318 "	25	5	5	100	99.4
1.172 "	25	1	10	100	92

The decomposition with sulphuric was much more rapid than with hydrochloric acid. When phenyl and ethyl arsonic acids were treated in the same manner only traces of arsenious acid were detected.

Decomposition of the Salts of Fatty Arsonic Acids by Heat.

It was found by Dehn (Am. Chem. Journ. 33, 133.), that heat decomposed magnesium ethyl arsonate into magnesium oxide, metallic arsenic, water and a hydrocarbon gas.

A closer study of this decomposition was made and it was found that the hydrocarbon gas was a mixture of methane and ethylene.

The unsaturated gas was separated from the methane by treatment with bromine water and their ratio was found to be in one case 42.5% of the former to 57.5% of the latter. A combustion on the residual gas gave the following:

43.5 c. c. of gas (corrected) equal to .0317 grams gave .0363 grams of CO_2 and 0.0714 grams of H_2O

Calculated for

	C H ₄	Found
C	75.00	75.10
H	25.00	24.04

An analysis of the saturated gas by the explosion method gave the following results:

Vol. gas saturated.	Vol.CO ₂ Theory	Vol.CO ₂ Found	Vol.H ₂ O Theory	Vol. H ₂ O Found
10.2	10.2	10.4	20.4	20.4
12.0	12.0	11.8	24.0	24.2

Evidently, the saturated gas is methane.

An analysis of the mixture of saturated (57.5%) and unsaturated (42.5%) gases was made by the explosion method and gave the following

Vol. gas	Vol.CO ₂	Vol.CO ₂	Vol.H ₂ O	Vol. H ₂ O
saturated and unsaturated	Calculated	Found	Calculated	Found
3.4	12.0	11.8	16.3	16.6
9.0	12.8	12.8	18.0	18.2

This indicates that the unsaturated gas is ethylene: an equation proposed to represent the decomposition of magnesium ethyl arsonate is as follows:



This cannot represent the entire reaction for water, is found as well as a larger amount of ethylene than is indicated by the equation. As magnesium ethyl arsonate is dehydrated and partially decomposed at 145° - 170° (Am. Chem. Journ. 33, 133.), the following secondary reaction may occur;



Furthermore as carbon dioxide, to the extent of 10 to 18 per

cent of the evolved gases and also metallic arsenic are formed amongst the decomposition products other reactions are probable.

Decomposition of Magnesium n-Propyl Arsonate by Heat.

When magnesium n-propyl arsonate was heated in an apparatus filled with carbon dioxide it yielded gaseous products, which when freed from carbon dioxide were soluble in bromine water to the extent of 40 %. Thus ^{the} gaseous products consists of 40 % of unsaturated hydrocarbon and 60 % of a residual gas whose analyses indicated a mixture of hydrogen with methane. In the analyses given below, the gas in experiment (a) was obtained from the total evolved gas while in experiment (b) the gas analyzed was obtained from the gas last evolved during the heating of the arsonate.

(a).	Vol. Gas	Vol.CO ₂ Found	Vol.H ₂ O Found	Vol.H ₂ O for Calculated H ₂	Vol.H ₂ O for Calc. Δ CH ₄	Vol.CO ₂ for Calc. Δ CH ₄
1.	15.0	8.6	25.4	15.0	30.0	15.0
2.	11.5	6.2	18.6	11.5	23.0	11.5
3.	12.0	6.9	19.8	12.0	24.0	12.0

This experiment shows that the saturated gas consists of nearly equal parts of hydrogen and methane.

(b)	Vol.Gas	Vol.CO ₂ Found	Vol.H ₂ O Found	Vol.H ₂ O for Calc. Δ H ₂	Vol.H ₂ O for Calc. Δ CH ₄	Vol.CO ₂ for Calc. Δ CH ₄
1.	10.8	7.8	14.1	10.8	21.6	10.8
2.	10.2	7.0	13.2	10.2	20.4	10.2
3.	10.7	7.3	13.7	10.7	21.4	10.7

This experiment shows about 70 % of methane.

When 40 grams of magnesium n-propyl arsonate were heated so that the gaseous products passed through bromine water, a quantity of

halogen-olefine addition product was obtained. Distillation of this oil yielded fractions that boiled near the boiling point of ethylene bromide (129.5°) and propylene bromide (141°).

Analysis of the fraction boiling near 129.5° gave the following data:

1. 0.2355 grams of substance required 0.4089 grams of AgNO_3 .
2. 0.2775 grams of substance required 0.4973 grams of AgNO_3 .
3. 0.3297 grams of substance required 0.5899 grams of AgNO_3 .

Calculated for

	$\text{CH}_2\text{BrCH}_2\text{Br}$	Found		
		1.	2.	3.
Br	85.11	85.35	84.35	84.20

Analysis of the fraction boiling near 141° gave this data :

0.2980 grams of substance required 0.4739 grams of AgNO_3 .

Calculated for

	$\text{C}_2\text{H}_5\text{BrCH}_2\text{Br}$	Found
Br	79.71	78.42

The evidence on the decomposition of magnesium n-propyl arsonate is too little at present to venture writing the equations involved.

Solubilities and Melting Points.

These properties of some of the arsonic and arsinic acids as determined by me are given in the accompanying table. The alcohol used was of 95% concentration.

Acid	Solvent	Temperature	Parts per 100	Melting Point
Ethyl Arsonic	H ₂ O	27 ⁰	70	99.5 ⁰
" "	"	40 ⁰	112	
" "	C ₂ H ₅ OH	25 ⁰	39.4	
Propyl Arsonic	H ₂ O	26 ⁰	43	125 ⁰
Isoamyl Arsonic	"	28 ⁰	.82	194 ⁰
" "	C ₂ H ₅ OH	21 ⁰	2.2	
Benzyl Arsonic	"	23 ⁰	.87	167 ⁰
" "	"	70 ⁰	5.91	
" "	H ₂ O	22.5 ⁰	.34	
" "	"	27 ⁰	.39	
" "	"	97 ⁰	3.50	
Phenyl Arsonic	"	28 ⁰	3.25	158 ⁰
" "	"	41 ⁰	4.82	
" "	"	52 ⁰	8.52	
" "	"	84 ⁰	24.00	
" "	C ₂ H ₅ OH	26 ⁰	15.51	
" "	"	68 ⁰	55.40	
Cacodylic	H ₂ O	22 ⁰	82.9	
Phenyl Arsinic	"	27 ⁰	.28	164 ⁰
" "	C ₂ H ₅ OH	22 ⁰	11.8	
" "	"	55 ⁰	57.7	

(1)

G. Meyers Reaction (Continued)

Continuing the work of Dehn the reactions of various haloid derivatives of the hydrocarbons with K_2AsO_3 were studied. In the reactions which are considered in the following table, the haloid derivative was used in excess of the theoretical amount.

<u>Haloid Derivative</u>	<u>Time</u>	<u>Temperature</u>	<u>% Yield</u>
Isobutyl Iodide	1 hr.	25 ⁰	5
"	4 "	25 ⁰	9
"	32 "	25 ⁰	10
"	48 "	25 ⁰	10
"	100 "	25 ⁰	10
"	1/2 "	80 ⁰	12
"	3 "	80 ⁰	12
"	1/2 "	80 ⁰	20
	3 "	25 ⁰	
Chloroform	1 "	25 ⁰	1
"	4 "	25 ⁰	1
"	45 "	25 ⁰	4
"	98 "	25 ⁰	4.8
Bromoform	1 "	25 ⁰	5
"	42 "	25 ⁰	15
"	53 "	24 ⁰	23
"	96 "	24 ⁰	30
"	140 "	24 ⁰	30
"	216 "	24 ⁰	30

<u>Haloid Derivative</u>	<u>Time</u>	<u>Temperature</u>	<u>% Yield</u>
Iodoform	26 hr.	23 ⁰	35.4
"	40 "	23 ⁰	50
"	51 "	23 ⁰	52.9
"	94 "	23 ⁰	79
"	114 "	23 ⁰	81.5
"	210 "	23 ⁰	92.2
"	1 1/2 "	80 ⁰	50
"	1 "	80 ⁰	51
"	1 1/2 "	80 ⁰	51
"	2 1/2 "	80 ⁰	54
"	2 1/2 "	80 ⁰	86.36
	15 "	25 ⁰	
p-Chlortoluene	1 "	23 ⁰	0
"	42 "	23 ⁰	3
"	96 "	23 ⁰	3
Allyl Iodide	10 min.	23 ⁰	39
"	30 "	23 ⁰	45
"	1 hr.	23 ⁰	46
"	26 "	23 ⁰	51

These determinations were made by titrating the K_2AsO_3 with standard iodine solution and thus determining the quantity which had been transformed. In the cases of isobutyl iodide and iodoform a slight quantity of K_2AsO_4 separated. The allyl iodide appeared to act abnormally, first a brown precipitate being formed and then a yellow oil.

Action of K_3AsO_3 on Iodoform.

As the titration method showed that iodoform reacted with K_3AsO_3 , an attempt was made to separate its reaction products. For this purpose 19 grams of iodoform were placed in a flask with 11.6 grams of K_3AsO_3 and 300 c. c. of alcohol, with just sufficient water to keep the arsenite in solution. The mixture was then heated for twenty minutes on the water-bath. After allowing to stand for four days the alcohol was removed by distillation and the residual aqueous solution was divided into two portions (a) and (b). An attempt was made to precipitate a magnesium salt, in the usual manner, by boiling with magnesi^{um} mixture, but it failed, no precipitate being formed. Solution (a) was then evaporated to dryness and the residue extracted with water so as to get rid of the excess of iodoform, which is insoluble in water. The aqueous extract was evaporated to dryness, the residue was extracted with alcohol and the alcoholic extract evaporated to dryness. This alcoholic extract was found to contain combined carbon and arsenic and upon reduction yielded an organic arsine. Tests showed that the arsenic was not present as arsenate or arsenite. The organic compound contained some halogen as determined with $AgNO_3$. The salt containing the organic carbon and arsenic could not be separated by extraction with 95% alcohol from the potassium iodide present, so that the second portion of the solution was used in the following manner. Solution (b) was reduced in an atmosphere of hydrogen with zinc and hydrochloric acid and the resulting organic arsine was passed into ether. After the ether had become saturated with the gas a light-yellow oil, heavier than ether, separated. The ether solution was left exposed to the atmosphere

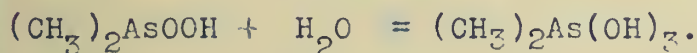
so as to oxidize the arsine to the corresponding arsonic acid, but the arsine was apparently very volatile and disappeared more readily than the ether. The reaction product was thus lost. It was, however, settled that a reaction takes place between potassium arsenite and iodoform with the formation of an organic arsenic compound which evidently contains halogen. It thus seems probable that some such compound as $\text{CHI}_2\text{AsO}(\text{OK})_2$ is formed by the reaction.

Bromoform reacts with potassium arsenite fairly well as shown by the preceding table but not nearly so readily as iodoform.

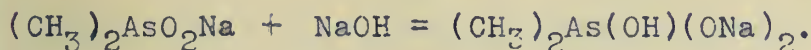
Chloroform reacts much more difficultly than either iodoform or bromoform. Time did not permit of further study of these reactions.

Electrical Conductivities of Arsonic and Arsinic Acids.

Hantzsch (Ber. d. chem. Ges. 37, 1076) concluded from his measurements of the conductivity of salts of cacodylic acid in water solution that the following equilibrium exists :



The mono-hydroxylated form functionates in the presence of metallic hydroxides giving salts of the type $(\text{CH}_3)_2\text{AsOOM}$; the trihydroxylated form functionates in the presence of an excess of alkali showing a weak tendency to form the salts of the type $(\text{CH}_3)_2\text{AsOH}(\text{OM})_2$:



Evidence for this conclusion is easily seen in the data submitted :

	Na Cacodylate	NaOH	<u>Na-Cacodylate + NaOH</u> By Addition Found		Differ- ence.
M ₁	56.8	202.0	258.0	232.8	25.2
M ₂	56.8	201.9	257.9	233.1	24.8

This effect is, however, very slight and entirely disappears in N/48 solution.

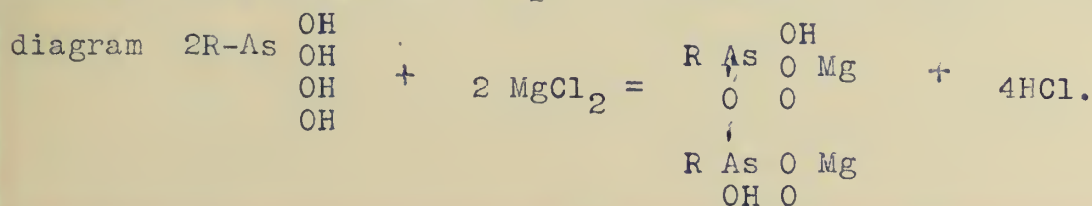
Hantzsch concludes further that cacodylic acid is an amphoteric electrolyte from the fact that it yields a chloride and a nitrate having formulas $(\text{CH}_3)_2\text{As}(\text{OH})_2\text{Cl}$ and $(\text{CH}_3)_2\text{As}(\text{OH})_2\text{NO}_3$ which are considered derived from the tri-hydroxylated form of cacodylic acid, $(\text{CH}_3)_2\text{As}(\text{OH})_3$. This amphoteric cacodylic acid being a "cacodylic alcohol" would be only slightly dissociated, as I have found by electric conductivities. The following conductivity measurements were made by Kohlrausch's method at $25^\circ\text{C}.$:

Molecular Conductivity.

V	M_1	M_2
1	.22	.22
2	.28	.28
4	.38	.37
8	.57	.57
16	.86	.86
32	1.35	1.35
64	2.35	2.34
128	3.35	3.35

It was found impossible to measure the conductivity in a more dilute solution than $n/128$. It is easily seen that the dissociation is much less than would be supposed, for it is known that cacodylic acid although a weak acid is much stronger than is indicated by the dissociation.

If, corresponding to $(\text{CH}_3)_2\text{As}(\text{OH})_3$, the arsonic acids form such compounds as $\text{RAs}(\text{OH})_4$, we might explain the presence of one half a molecule of H_2O in the magnesium salt by the following



This reaction-product when written empirically would correspond in composition to $(\text{RASO}_3\text{Mg})_2\text{H}_2\text{O}$ which has been found to be correct with some of the arsonic acids. Walden (Zt. Phys. Chem. 1,533.) has measured the conductivity of the magnesium cacodylate and has found that dissociation shows no signs of completion in n/1024 solution, thus emphasizing the extreme weakness of cacodylic acid in water solution at the usual concentration. The conductivity of ethyl arsonic acid was likewise measured and though much greater than that of cacodylic acid it was very evident that dissociation in n/1024 solution did not approach completion. Whether this slight dissociation in water solution is due to the formation of $\text{RAS}(\text{OH})_4$, as suggested above in the formation of the magnesium salt, has not been determined.

The conductivity of ethyl arsonic acid as measure by Kohlrausch's method at 25°C . is given in this table.

V	<u>Molecular Conductivity.</u>	
	M_1	M_2
1	2.33	2.34
2	3.13	3.15
4	4.23	4.24
8	5.98	5.98
16	8.27	8.24
32	11.49	11.43
64	16.17	15.98
128	23.10	23.03
256	33.01	32.81
512	46.93	46.37
1024	65.25	64.94

In conclusion I wish to thank Dr. Wm. M. Dehn for his untiring advice and assistance.

Approved by
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